

RATIONALE FOR DETERMINATION OF MACT FOR INDIRECT-FIRED PROCESS HEATERS

TABLE OF CONTENTS

Section	Content	Page
I.	Executive Summary	2
II.	Overview of the MACT Determination Process for Process Heaters	3
II.A	- Review Process Heater Inventory Databases	3
II.B	- Compile Process Heater Emissions Information	3
II.C	- Select Sources for MACT Rulemaking	4
II.C.1	+ Eliminate Direct-Fired Process Heaters	4
II.C.2	+ Eliminate Indirect-Fired Process Heaters Regulated Under Another MACT	5
II.D	- Subcategorize Sources by Fuel Type	5
II.E	- Evaluate Controls and Emissions Information	6
II.F	- Consider Pollution Prevention Guidance	6
III.	Analysis of Process Heater Inventory Database	6
III.A	- Overview of Population Data	6
III.B	- Analysis of Control Data	7
IV.	Overview of Process Heaters Emissions Information	8
V.	MACT Determination for the Process Heater Gas Fuel Subcategory	10
V.A	- Fuel Type vs. HAPs	10
V.B	- Operating Load vs. HAPs	11
V.C	- Stoichiometric Ratio vs. HAPs	11
V.D	- NO _x Control Equipment vs. HAPs	12
V.E	- Operating, Maintenance, and P2 Planning Practices vs. HAPs	13
V.F	- Process Heater Design vs. HAPs	15
V.G	- State Regulations and Permits	15
V.H.	- Process Heater MACT Determination for the Gas Fuel Subcategory	15
VI.	MACT Determination for the Process Heater Fuel Oil Subcategory	16
VII.	MACT Determination for the Process Heater Residual and Crude Oil Subcategory	17
VIII.	MACT Determination for the Process Heater Wood Fuel Subcategory	18
IX.	MACT Determination for the Process Heater Coke Oven Gas Fuel Subcategory	18
X.	Discussion on Emissions Variability	19

I. Executive Summary

This document provides the rationale for the recommended determination of Section 112 MACT for indirect-fired process heaters. Units regulated under Section 112 of the Clean Air Act are within the scope of this document; units regulated under Section 129 (solid waste incinerators) are not.

This document represents a summary of two years of intensive work by the ICCR Process Heater Work Group, during which time a rigorous and detailed evaluation of MACT for this source category was conducted. In fact, critical work on this source category actually commenced as far back as 1992 with the initiation of the PERF 92-19 "Toxic Combustion Byproducts" project. The Process Heater Work Group consisted of a cross-section of stakeholders including representatives from aluminum, coke and coal chemicals, environmental citizens groups, environmental consultants, forest and paper, grain and feed, petroleum, petrochemical, state environmental agencies, and the EPA's Office of Air Quality Planning and Standards and Office of General Counsel.

In this paper a MACT floor determination for existing sources of "no control" means that, based on the data currently available, no group corresponding to the best performing 12% of existing sources could be identified by reviewing the following information:

- Existing add-on controls that may reduce HAPs.
- Existing combustion practices that may reduce HAPs.
- Existing emissions data, air regulations, and air permit limitations for HAPs.

A MACT above-the-floor determination of "no control" means that no stack controls or combustion practices could be identified that reduce HAPs in a cost-effective manner. Additionally, a MACT floor determination for newly constructed sources of "no control" means that a review of the above items identified no add-on controls, no combustion practices, and no other measures currently in place to reduce HAPs on any source.

Based upon the MACT evaluation process described in detail in this paper, the current MACT floor and above-the-floor determinations for indirect-fired process heaters are summarized as follows:

Table 1. Summary of MACT Determinations for Indirect-Fired Process Heaters

<u>Subcategory</u>	<u>No. of Units in Database</u>	<u>MACT Floor for Existing Sources</u>	<u>MACT Floor for New Sources</u>	<u>MACT Above the Floor</u>
Gas	14513	No control	No control	No control
Fuel Oil	750	No control	No control	No control
Residual/Crude Oil	354	No control	To be determined	To be determined
Wood	36	To be determined	To be determined	To be determined
Coke Oven Gas	18	No control	To be determined	To be determined
Other	63	To be determined	To be determined	To be determined

These determinations were made by the Process Heater Work Group for presentation to the Coordinating Committee. They do not represent actual regulatory decisions. Such decisions will be made by EPA.

II. Overview of the MACT Determination Process for Process Heaters

The Work Group used a six-step process in its approach to determining the MACT standard for process heaters.

- A. Review the inventory databases to identify the sources to be considered in the MACT determination.
- B. Compile emissions data for the sources identified in the inventory.
- C. Select the sources for MACT rulemaking.
- D. Subcategorize the sources by fuel type.
- E. Evaluate controls and emissions information.
- F. Consider pollution prevention guidance.

II.A Review Process Heater Inventory Databases

Conclusion: The process heater inventory database was developed from existing electronic databases, and from a Section 114 Information Collection Request.

The ICCR Inventory Process Heater Database V.3 was used as the basis for the MACT determinations. This inventory database is a compilation of information made available from existing electronic databases such as AIRS, OTAG, and from state and local agencies. This database includes information on location, combustor description and application, fuel description, size, hours of operation, and other operating parameters for each process heater.

In addition to the ICCR Inventory Database, information was made available as a result of a Section 114 Information Collection Request. The primary purpose of this survey was to obtain additional information concerning the population and emissions from devices that combust material other than fossil fuels. The results of the ICR were compiled in a Survey Database V.2 for use along with the ICCR Inventory Database information.

II.B Compile Process Heater Emissions Information

Conclusion: The process heater emissions database was developed from existing electronic databases, from a Section 114 Information Collection Request, from source test results collected under the California Air Toxics "Hot Spots" Inventory and Assessment Act and compiled by WSPA/API, and from the Petroleum Environmental Research Forum (PERF) 92-19 "Toxic Combustion Byproducts" project.

The ICCR Emissions Process Heater Database V.2 used in the MACT

determination process originated from three primary sources. First, this emissions database is a compilation of information made available from existing electronic databases such as STIRS, and from state and local agencies. Emissions information collected from the 114 ICR survey was also added to this database.

Secondly, source test results collected under the California Air Toxics "Hot Spots" Inventory and Assessment Act (AB2588) have been compiled and quality reviewed in a joint effort by the Western States Petroleum Association (WSPA), the California Air Resources Board (CARB), and the American Petroleum Institute (API). A presentation on this database was provided to the ICCR work group members on November 18, 1997. Additional source test data from two California refineries have been added to this database post the November, 1997 review.

These data are documented in a September 22, 1997 report entitled "Development of Toxics Emission Factors for Petroleum Industrial Combustion Sources" by D. W. Hansell and G. C. England that is available in the ICCR docket. The validation and verification processes used to quality assure these data make this the most reliable and comprehensive compilation of field emission source test data for petroleum industry combustion sources.

The third source of emissions test data came from the Petroleum Environmental Research Forum (PERF) 92-19 "Toxic Combustion Byproducts" project. In 1992 PERF initiated a Cooperative Research and Development Agreement (CRADA) with the U.S. Department of Energy, and with EPA participation, performed an experimental and fundamental investigation of chemical and physical mechanisms governing organic HAP formation, destruction, and emissions. These tests on full-scale burners were performed at the Sandia National Laboratories/Livermore.

This program produced data of very high quality that shed light on many of the key questions surrounding the field data. The results of this project were presented to the Coordinating Committee on July 22, 1997, and are summarized in a July 16, 1997 paper by G. C. England and D. W. Hansell entitled "Organic Hazardous Air Pollutant Emissions from Gas-Fired Boilers and Process Heaters" that is available in the ICCR docket. The PERF 92-19 CRADA Final Report, "The Origin and Fate of Toxic Combustion Byproducts in Refinery Heaters: Research to Enable Efficient Compliance with the Clean Air Act" (August 5, 1997), is available to the public at <http://www.epa.gov/ttn/iccr/dirss/perfrept.pdf>. The complete 10-volume study including test reports and appendices has been placed in the ICCR docket.

II.C Select Sources for MACT Rulemaking

Conclusion: Direct-fired process heaters, and indirect-fired process heaters regulated under another MACT, were eliminated from the scope of the determination.

II.C.1 Eliminate Direct-Fired Process Heaters

Both direct- and indirect-fired process heaters were included in the initial scope of the ICCR. "Direct-fired" process heaters are those in which the products of

combustion mix with process materials and the combined emissions exit the same stack. By contrast, "indirect-fired" process heaters are those in which the emissions arise solely from products of combustion. EPA has established separate rulemaking projects for development of MACT standards for most if not all of these direct-fired process heaters, and the Coordinating Committee has recognized that direct-fired process heaters will be addressed in these projects.

Following a presentation by the Process Heater Work Group to the Coordinating Committee on February 24, 1998, the Coordinating Committee forwarded recommendations to EPA that the ICCR focus on indirect-fired process heaters [March 27, 1998 letter from R. F. Anderson and F. L. Porter to R. D. Wilson]. If in the course of review and deliberations, a category of direct-fired process heaters that would not otherwise be addressed by the EPA is identified that appears to be an appropriate candidate for MACT standards, then this category could be considered for inclusion in the ICCR. No such category has been identified to date.

A list of these direct-fired units by SCC code was presented on March 19, 1997 to the Coordinating Committee and an updated version of these tables is available in the ICCR docket.

II.C.2 Eliminate Indirect-Fired Process Heaters Regulated Under Another MACT

In addition to segregating out direct-fired process heaters, the Coordinating Committee agreed to recommend to EPA that regulation of any indirect-fired process heaters that fall under another MACT category or standard would be left to that project. A list of these units by SCC code was presented on March 19, 1997 to the Coordinating Committee, and an updated version of these tables is available in the ICCR docket.

II.D Subcategorize Sources by Fuel Type

Conclusion: Sources were subcategorized by fuel type.

As described in more detail in Sections III.A and B, based upon the inventory and emissions data available, the Process Heater Work Group took the approach of subcategorizing the process heaters remaining in this category by fuel type. The category was divided into the following subcategories: (1) gas, (2) fuel oil, (3) residual and crude oil, (4) wood, (5) coke oven gas, and (6) other.

For the purposes of these subcategories, gas is defined as follows:

- (1) A naturally occurring mixture of hydrocarbon and non-hydrocarbon gases found in geologic formations beneath the earth's surface, of which one of the principal constituents is methane;
- (2) Liquid petroleum gas, as defined by the American Society of Testing and Materials in ASTM D1835-82, Standard Specification for Liquid Petroleum gases.
- (3) Gaseous fuel derived from the processing of crude oil, petroleum, or

petrochemicals.

II.E Evaluate Controls and Emissions Information

Conclusion: MACT determinations for each subcategory were performed using the inventory and emissions databases.

The ICCR Process Inventory Database was used to determine the percentages of sources in each of the subcategories that were equipped with HAP controls. This required a careful analysis of the database to be certain that the information provided in fact represented add-on devices or operating practices that actually control HAPs on indirect-fired process heaters. This information was then used to determine whether a MACT floor could be defined for existing as well as new sources. If in fact actual HAP controls could be identified, then an above-the-floor analysis which considered the cost and resulting benefits of such controls would be conducted on these controls.

The available HAPs emissions information was also used to determine if a best performing 12% of sources within each subcategory could be identified. Where available, these data were used to look at the relationship between add-on controls, design parameters, and operating variables to determine if in fact a relationship exists between these factors and HAP emissions.

II.F Consider Pollution Prevention Guidance in MACT Evaluation

Conclusion: Pollution prevention aspects were considered in determining MACT.

The Coordinating Committee asked the Workgroups to consider pollution prevention (P2) aspects, where appropriate, when performing their MACT determinations. The P2 guidance provided by the Coordinating Committee to the Workgroups addressed the following aspects:

- Good combustion/operating practices
- Operator training/qualification
- Metrics which encourage pollution prevention
- Waste accounting, record keeping, and work practice standards
- Fuel/waste constituent and de minimus levels
- Alternative compliance provisions
- Pollution prevention planning

As described in Section III.C.6, the Process Heater Work Group considered each of these aspects, where applicable.

III. Analysis of Process Heaters Inventory Database

III.A. Overview of the Population Data

Conclusion: A thorough review of the inventory databases available showed that

these databases are representative of all process heaters and adequate for determining MACT. Gas-fired units represent approximately 85% of the process heaters in the database.

As discussed in Section II.A, the ICCR Process Heater Inventory Database V.3, and the ICR Survey Database V.2 were reviewed as part of the Process Heater Work Group MACT determination effort. It was determined that an estimated 20-30% of the process heaters in the U.S. are included in this database. A detailed review of this information led the Work Group to conclude that the information on process heater characteristics (e.g. fuel type, design, firing rate, application, etc.) is representative of all process heaters used throughout industry, and consequently adequate for determining MACT.

The analysis involved removing from the initial list of over 32,000 process heaters those that were direct-fired process heaters, duplicates, indirect-fired process heaters covered by other MACTs, and misclassified units/errors. This resulted in a total of 17,207 remaining process heaters for further analysis. As shown in the flow diagram "ICCR Process Heater Database Analysis Flow Diagram" attached at the end of this document, these remaining heaters were subdivided into fuel subcategories as follows: 14531 gas (18 of which are coke oven gas), 750 fuel oil, 354 residual and crude oil, 36 wood, 63 other, and 1473 fuel unspecified. Not surprisingly, gas-fired process heaters represent about 85% of the total process heaters. The combination of gas and fuel oil-fired process heaters represents approximately 89% of the total.

III.B. Analysis of Control Data

Conclusion: No controls that impact HAP emissions have currently been identified for any of the fuel subcategories with the exception of wood-fired sources. Further analysis of the wood-fired source control data is required.

As discussed in Section III.A, a total of 17,207 possible indirect-fired process heaters remained in the database for further analysis. A detailed evaluation of the available information on these process heaters and their associated controls was then performed.

Of the process heaters that indicated controls, most of these controls were low NO_x burners which as discussed later in Section V.D have no impact on HAP emissions. Secondly, the process heaters which indicated controls such as ESPs, bag houses, and fabric filters, upon further analysis turned out to be direct-fired units, or misclassified units such as incinerators. It was also discovered that some of these controls were in fact controlling emissions from a stack on the process reactor or vessel, and not on the process heater associated with that operating unit.

Lastly, there was so little information available on the devices in the fuel unspecified subcategory that it was not possible to identify the actual fuel being burned, the type or name of the facility, or a contact person. The Work Group therefore made a consensus decision to eliminate the fuel unspecified sources from further analysis.

Consequently, as summarized below in Table 2, of the 914 "controlled" process heaters, it was determined that only a few of these controls were in fact controlling HAPs on indirect-fired process heaters. While still under evaluation, it appears that most if not all of these controls are confined to the wood subcategory. As discussed in the "ICCR Process Heater Work Group "Other"-Fired Status Report", this subcategory is undergoing further control analysis to determine whether a MACT floor can be established. Supporting information on each of the sources reviewed in this refined analysis is currently being documented.

Table 2. Number and Percent of Controlled Process Heaters

Fuel Type	Gas	Coke Oven Gas	Fuel Oil	Residual/ Crude Oil	Wood	Other*	Fuel Un- Specified	Total
Total	14513	18	750	354	36	63	1473	17207
No. Indicating Controls	813	9	38	25	22	7	353	914
No. Controlled for HAPs	0	0	0	TBD	22	TBD	--	TBD
Percent Controlled	0	0	0	TBD	61	TBD	--	<0.5

TBD = To Be Determined

*includes coal, other gas, other liquid, and other solid

IV. Overview of Process Heater Emissions Information

Conclusion: Process heater emissions information consists of both validated source tests under a wide range of field operating conditions, and high quality full-scale burner tests conducted under the Petroleum Environmental Research Forum (PERF) 92-19 "Toxic Combustion Byproducts" project. The information on gas-fired sources is extensive and represents the majority of the available emissions data. Results from the boiler emissions database have been used to supplement data on emissions from fuel and residual oil combustion. As predicted by the PERF study, field results show very low levels of HAP emissions from these sources.

As discussed in Section II.B, the available process heater emissions information consists of both validated source tests collected under a wide range of field operating conditions, and high quality full-scale burner tests conducted under the Petroleum Environmental Research Forum (PERF) 92-19 "Toxic Combustion Byproducts" project. Table 3 lists the number of emission data points for various key constituents that are available in the emissions database.

Table 3. Number of Available Emission Data Points for Various Key Constituents

Subcategory	Constituent	Number of Emission Data Points			
		ICCR	WSPA	PERF	Total
Gas	Benzene	21	59	58	138
	Formaldehyde	6	47	58	111
	PAH	10	40	29	79
Fuel Oil ¹	Benzene	3	--	--	3
	Formaldehyde	3	--	--	3
	PAH	3	--	--	3
Residual and Crude Oil ¹	Benzene	56	6	--	62
	Formaldehyde	66	6	--	72
	PAH	46	3	--	49
Wood	Benzene	--	--	--	--
	Formaldehyde	--	--	--	--
	PAH	--	--	--	--
Coke Oven Gas	Benzene	--	--	--	--
	Formaldehyde	--	--	--	--
	PAH	--	--	--	--

As can be seen in the table, extensive information exists on gas-fired process heaters, and consequently as explained in detail in Section V, emissions from this subcategory are well categorized. There is, however, less information available on the other fuel types. This is not surprising as these fuels represent a much smaller fraction of the fuels being fired as compared to gas. This is particularly true in California, which is the source for much of the HAP emissions testing. Where available, emissions data from boilers firing these other fuels have been used to supplement the Work Group's analyses. Based upon a comparison of the emission factors presented in the WSPA/API database, these data are believed to be representative of emissions from process heaters firing these fuel types.

As discussed in more detail in the sections that follow, these data demonstrate that the results from field and PERF laboratory tests are similar, and that the emissions from process heaters firing many of these fuels are at or near the limits of detection. For example PAHs, if detected at all, were measured in the range of 1E-07 to 1E-05 ppm.

The very low level of HAP emissions from these sources is illustrated in Table 4 for gas-fired process heaters. Using the mid-range factors in this table, the emissions of these three categories of constituents from a 100 MMBtu/hr process heater would only total approximately 0.04 tons per year. For a facility firing 5000 MMBtu/hr this total would equate to approximately two tons per year.

¹ Includes results from the boilers emissions database, as these are believed to be representative of emissions from process heaters firing these fuel types.

Table 4. Approximate HAP Emission Factors for Key Constituents from Gas-Fired Process Heaters

Subcategory	Constituent	Approximate Emission Factor, lb/MMBtu		
		Low Range	Mid Range	High Range
Gas	Benzene	1E-07	1E-05	1E-04
	Formaldehyde	1E-06	1E-05	1E-03
	PAH	1E-08	5E-08	1E-06

V. MACT Determination for the Process Heater Gas Fuel Subcategory²

Conclusion: After fully evaluating the inventory and emissions data available, it is not possible to identify a "best performing" subset of existing sources. No discernable relationships were identified between HAP emissions from gas-fired process heaters and fuel type, operating load, stoichiometric ratio, NOx controls, design parameters, or operating, maintenance, and pollution prevention planning practices. As a result, the Work Group believes that there is no MACT floor, nor any above-the-floor controls, for existing and new process heaters in this subcategory.

V.A Fuel Type vs. HAPs

Conclusion: There is no discernable difference in HAP emissions from process heaters firing natural gas, refinery/process gas, or combinations of these gases.

Process heater benzene, formaldehyde, and PAH emissions from natural gas, refinery/process gas, and combinations of these gases are shown in Figures 1-3. Field data from the WSPA/API and the ICCR databases are plotted, along with the results of the full-scale PERF laboratory studies. The emissions are reported in pounds per million Btu (lb/MMBtu). The fuel type description and data source, and the total number of data points in each group, are noted on the x-axis. A data point is a single test run, and normally there are three test runs per each sampling event on any given heater.

It should be mentioned that the PERF study looked in detail at differences in fuel type/quality, (i.e. differences in composition, molecular weight, heating value, etc.) and found no correlation with HAP emissions. For the purpose of these figures, these different fuel "types" are combined together and shown as either natural gas or refinery gas.

These data indicate that there are no discernable differences in organic HAP emissions from process heaters fired with various gaseous fuels. In addition, the results demonstrate that the emissions data in the ICCR, API/WSPA, and PERF databases are comparable and fall within the same range of emissions.

² Emissions data from the PERF study for test conditions with a stoichiometric ratio (SR) less than one and three and greater were removed from the databases for these analyses. These were extreme test conditions carried out for fundamental scientific purposes that are not representative of process heater operating conditions.

V.B Operating Load vs. HAPs

Conclusion: There is no discernable relationship between operating load and HAP emissions for process heaters.

Operating load was determined from data in the WSPA/API and ICCR source test reports and is defined as the average firing rate during the source test, expressed as percent of design capacity.

Figures 4-6 contain benzene, formaldehyde, and total PAH emissions, respectively, versus operating load for gaseous fuels from the API/WSPA and ICCR databases. These figures clearly demonstrate that, as expected, there is no discernable relationship across the population of process heaters between operating load and HAP emissions. No HAP emissions data were available on individual process heaters as a function of change in load. However, based on the population data, no relationship is expected.

The PERF data could not be used in the analysis of impact of load since adjustments in load during the PERF test program also included very large changes in the stoichiometric ration (SR). The impact of load on HAP emissions was not an element of the PERF study, therefore the impacts of SR and load on HAPs emissions can not be cleanly decoupled. Nevertheless, looking at the various load conditions in the PERF test program, the same conclusion is obtained; *viz.*, there is no dependence of HAP emissions on load.

V.C Stoichiometric Ratio vs. HAPs

Conclusion: There is no discernable relationship between stoichiometric ratio and HAP emissions within the expected SR operating range for process heaters.

The impacts of stoichiometric ratio³ on benzene, formaldehyde, and total PAH for gaseous fuels are illustrated, respectively, in Figures 7-9. These data came from the WSPA/API, ICCR, and PERF databases. Since detailed fuel composition information was not available for the field source test data, average compositions (C, H, N, O content) for gaseous fuels along with stack gas oxygen content were utilized to calculate the SR. Large changes in fuel properties have minimal impact on this calculation so this method provides a good estimate of SR. It is not possible to account for any dilution air that is introduced into the system downstream of the combustion zone.

These figures show that the vast majority of process heaters in the emissions database operate at a SR between 1 and 2. Operating a process heater in the sub-stoichiometric range (SR<1) is extremely dangerous in that it can result in burner flame-out. This can lead to an accumulation of combustible gases in the firebox that can result in an explosion and/or fire, a condition that facilities go to great lengths to avoid. Only two

³ Stoichiometric Ratio is equal to the mass flow rate of air that is actually provided to the burner divided by the mass flow rate of air that is theoretically required for complete combustion. A SR of 1 to 2 is approximately equivalent to the following: (a) 0%<stack O₂<11%, (b) 0%<excess air <100%, (c) 100%< theoretical air <200%.

process heaters (one with detectable emissions) were reported operating at a SR above 2. While not a safety issue, operating above a SR of 2 is undesirable because it is uneconomical and wasteful of fuel. Additionally, many facilities/process heaters now operate under NO_x permit limits. These limits can be difficult to meet if the device is operating at a SR above 2.

These figures also demonstrate that within this SR operating range, there is no discernable correlation between SR and HAPs emissions. Neither the WSPA/API field data, the ICCR field data, nor the results of the PERF study suggest that there is any relationship between SR and HAPs within the expected SR operating range for process heaters.

While not shown on these graphs it should be noted that, for fundamental scientific purposes, the PERF study did look at SR extremes that are not normally found in actual process heater operation. As virtually no HAPs had been detected during the PERF tests when conducted in the normal SR operating range, the PERF researchers decided to run some extreme cases in order to be sure they could generate and in particular measure the HAPs created. Several PERF laboratory tests were run at SR's less than 1 (0.4 to 0.8) and at 3 and 4.5. As expected, the PERF study found that for these extreme combustion conditions, emissions of benzene, formaldehyde, and PAH increased to levels in some cases substantially above those shown in these figures.

V.D NO_x Control Equipment vs. HAPs

Conclusion: NO_x control equipment has no discernable effect on HAP emissions from process heaters.

Comparisons of HAP emissions for process heaters with various forms of NO_x control equipment are shown in Figures 10-12. The combustion and downstream NO_x control equipment found on the tested units includes low NO_x burners (LNB), selective catalytic NO_x reduction (SCR), and selective non-catalytic NO_x reduction (SNCR). The information used in these Figures came from the WSPA/API and PERF data sources. The ICCR database did not include enough specific information on NO_x control equipment to be included in this analysis.

As can be seen in these Figures, the emissions of benzene, formaldehyde, and PAH are comparable regardless of whether the heater was equipped with any type of NO_x control device.

V.E Operating, Maintenance, and P2 Planning Practices vs. HAPs

Conclusion: There is little opportunity, if any, to reduce HAP emissions through changes in operating, maintenance, and pollution prevention planning practices.

Operator Knowledge, Training, and Documentation of Procedures

Due to safety, economic, and operational reliability and integrity concerns, the operation and maintenance of process heaters at most facilities requires a high level of operator knowledge, training, and procedural documentation. Process heaters are often important elements in manufacturing processes, and their performance is critical in providing a safe, reliable, and economically sound operation.

Proper operation and maintenance of a process heater will help ensure optimum performance over its lifetime. Manufacturers recommend operation and maintenance (O&M) procedures to establish the parameters under which their warranty for the equipment would be valid. These procedures are designed primarily to avoid equipment damage rather than to control emissions, but recognize that proper operation and maintenance will usually maintain good combustion efficiency.

These O&M procedures contain sections on preventive and corrective maintenance. While owners/operators may customize these manufacturer-recommended procedures due to updated information or to recognize site-specific conditions, such as extreme ambient temperature fluctuations or remote automated operations, ignoring or neglecting service/maintenance procedures will have an adverse impact on the performance and life of the process heater.

Operators, as part of their internal O&M procedures, also specify training and/or qualification requirements from a safety, performance, reliability, service/maintenance, and equipment warranty perspectives. Established company training programs also specify the ground-rules by which an apprentice advances to a mechanic or a technician level, a prerequisite to operating multi-million dollar equipment. Other programs, such as OSHA and Process Safety Management (PSM), address operator training programs and requirements.

Consequently, new additional regulatory language is not necessary to prompt facilities to protect their significant capital investment and business interests and, thereby, minimize emissions by ensuring that their operators are properly and adequately trained, and procedures documented. Any such requirements would be duplicative and result in an unnecessary burden to plant operating personnel.

Operating Practices

As demonstrated throughout this report, HAP emissions from process heaters are unchanging over a wide range of operating conditions. No correlation between operating conditions and HAPs has been identified for any operating parameter within the expected operating range of process heaters.

Fuel Quality

As discussed earlier, the PERF study looked at differences in fuel quality, i.e. differences in composition, molecular weight, and heating value, and found no correlation with HAP emissions.

The fuel quality, whether in terms of heating value, molecular weight, entrained impurities such as water and heavy hydrocarbons, etc. is specified by the process heater design. Continued use of fuel outside of that specified by the designer can result in degradation of performance, and therefore the operator will quickly correct this situation. Consequently, a facility's vested business interest in protecting its capital investment and maintaining operational integrity will dictate that particular attention be paid to the fuel quality and any resulting lack-of-performance issues.

In situations where a process heater is used as a combustion control device on a particular process vent stream, the HAP emissions from the heater are regulated (to the best of our knowledge) by the process-specific MACT standard governing that operation. This is certainly the situation for the petrochemical and petroleum industries. For example, the MACT standard applicable to the Synthetic Organic Chemical Manufacturing Industry, also referred to as the Hazardous Organic NESHAP or HON, has specific requirements for both halogenated and non-halogenated vent streams that are combusted in process heaters. These requirements are found in 40 CFR Part 63 Subpart G. Another example of provisions for controlling (non-halogenated) vent streams can be found in 40 CFR Part 63 Subpart CC - NESHAPs for Petroleum Refineries.

Pollution Prevention Planning

Pollution prevention planning as it applies to process heaters could involve looking at the characteristics of the fuel, the efficiency of the combustion device itself, as well as determining if the energy produced onsite by the combustion device is being efficiently utilized. As described in the "Pollution Prevention Planning Requirements" document developed by the P2 subgroup, the process is driven by the facility. It involves conducting various energy efficiency audits, identifying potential efficiency steps, then evaluating these steps to determine if there is justification to pursue any of them.

This kind of process can be justified in situations where (1) changes in efficiency can result in significant reductions in HAPs or other pollutants, (2) market forces work against energy conservation, and (3) there has been little if any regulatory pressure to reduce emissions or wastes.

The situation for gas-fired process heaters fails to meet any of these criteria. Due to the very low emissions of any type from these sources, and the economic and competitive pressures that mandate highly efficient fuel consumption, there is little opportunity to further reduce HAPs emissions through improvements in device and energy utilization efficiency. Existing regulations and controls on NO_x emissions also require that the device be operated at high fuel efficiency.. Consequently, there is little opportunity to

make meaningful reductions in emissions through new and different pollution prevention technologies for these sources.

V.F Process Heater Design vs. HAPs

Conclusion: Process heater firebox design parameters (i.e. residence time, temperature, and turbulence) have no relevance to HAP emissions.

The Process Heater Work Group discussed the potential impact of the firebox design parameters. Unlike an incinerator where firebox residence time, temperature, and turbulence are critical parameters for ensuring complete combustion, these parameters are irrelevant for process heaters.

This is because the processes of fuel/air mixing and HAP formation and destruction, occur within the flame zone and not the firebox. Process heaters are designed with high temperature jet-mixed burners which ensure that all of the reactions occur at temperatures, mixing regimes, and residence times far in excess of what is required to ensure HAP destruction.

As discussed in this report, the PERF study as well as the field data have confirmed that the jet-mixed combustion process is extremely robust, producing predictable, exceedingly low emissions of HAPs over a broad range of operating conditions. While there is very little design-related information in the WSPA/API and ICCR databases, for the reasons stated here the Work Group does not believe that such information is relevant to HAP emissions from process heaters. Additional detail on these aspects can be found in the PERF study report referenced earlier.

V.G State Regulations and Permits

Conclusion: Currently, no state regulations have been identified which limit specific HAP emissions from indirect gas-fired process heaters.

Another aspect that was considered in the MACT determination process was the utilization of existing state regulations and permits. Regulatory programs in various states were evaluated to see if HAP emissions limitations exist for indirect gas-fired process heaters. Currently, no state regulations have been identified which limit specific HAP emissions from these heaters. The few instances (e.g., Texas) where a specific limit for a HAP (e.g., benzene) has been imposed, the process heater has not been the HAP source, but rather the control device.

V.H Process Heater MACT Determination for the Gas Fuel Subcategory

Existing Sources: After fully evaluating the inventory and emissions data currently available, a "best performing" 12% of existing sources could not be identified. There are no relationships that can be identified between HAP emissions and add-on controls, combustion, operating and maintenance practices, design parameters, and state air regulations and permit limitations. As a result, the Work Group believes that there is

no MACT floor, nor any above-the-floor controls, for these sources.

It should be added that various recent reports including EPA's "Electric Utility Hazardous Air Pollutant Study Final Report to Congress" (Fed. Reg. Vol. 63, No. 41, March 3, 1998) support the facts that the risks associated with emissions from these sources are believed to be "negligible".

New Sources: As stated above, no design, operating and maintenance, or stack control parameters have been demonstrated to further reduce HAP emissions. As a result, the Work Group believes that there are no MACT controls for new sources.

VI. MACT Determination for the Process Heater Fuel Oil-Fired Subcategory

Conclusion: After fully evaluating the inventory and emissions data currently available, a "best performing" 12% of existing sources could not be identified. While the emissions data are limited, there are no relationships that can be identified between HAP emissions and add-on controls, combustion, operating and maintenance practices, design parameters, and state air regulations and permit limitations. As a result, the Work Group believes that there is no MACT floor, nor any above-the-floor controls, for these sources.

Based on the analysis of the process heater inventory database described in Section III.B, no best performing 12% of existing sources could be identified for this subcategory based on existing add-on controls.

With respect to a MACT floor determination based on emissions information, there are no HAP emissions data from fuel-oil fired process heaters, and only three data points from fuel-oil fired boilers, in the emissions database on which to base such an analysis. This is not surprising as relatively few process heaters utilize fuel oil⁴. This is most notably the case for California, which provided the majority of the sources in the WSPA/API emissions database. There are, however, some additional limited data in the published literature on HAP emissions from boilers firing fuel oil (Miller, C. Andrew, *et al*, J.AWMA, v.46, August 1996). Taken together, these data indicate that in general, HAP emissions from fuel oil-fired devices are similar to or in some cases slightly higher than those from gas fired sources.

Given the lack of emissions data, it was not possible to perform a detailed analysis of HAP emissions versus parameters such as fuel type, operating load, stoichiometric ratio, etc. as was done for the process heater gas subcategory. However, one would expect the same results and conclusions to apply to fuel oil as to gas. This is because fuel oil is easily atomized to a gas and, therefore, the products of combustion are expected to be gas-like. With the exception of the atomization step, a process heater firing fuel oil would be expected to behave in a manner very similar to one firing gas. Consequently, the conclusions reached for gas-fired process heaters as described in

⁴ For the purposes of this subcategory, fuel oil is considered to be No. 4 oil or lighter.

Sections V.A through V.G are believed to hold as well for fuel oil-fired process heaters.

Existing Sources: After fully evaluating the inventory and emissions data currently available, a "best performing" 12% of existing sources could not be identified. There are no relationships that can be identified between HAP emissions and add-on controls, combustion, operating and maintenance practices, design parameters, and state air regulations and permit limitations. As a result, the Work Group believes that there is no MACT floor, nor any above-the-floor controls, for these sources.

New Sources: As stated above, no design, operating and maintenance, or stack control parameters have been demonstrated to further reduce HAP emissions. As a result, the Work Group believes that there are no MACT controls for new sources.

VII. MACT Determination for the Process Heater Residual and Crude Oil⁵-Fired Subcategory

Conclusion: After fully evaluating the inventory and emissions data currently available, a "best performing" 12% of existing sources could not be identified. As a result, at this time there appears to be no MACT floor for this subcategory. An above-the-floor analysis for this subcategory, including pollution prevention aspects, has not yet been conducted.

Based on the analysis of the process heaters inventory database described in Section III.B, no best performing 12% of existing sources could be identified for this subcategory based on existing add-on controls.

With respect to a MACT floor determination based on emissions information, there are very few HAP emissions data from residual and crude oil fired process heaters in the emissions database on which to base such an analysis. This is not surprising, as very few process heaters routinely utilize these fuels. This is most notably the case for California, which provided the majority of the sources in the WSPA/API emissions database.

However, the ICCR emissions database does contain a fair amount of HAP emissions data from industrial boilers firing fuel oil. These data indicate that, in general, organic HAP emissions from residual oil-fired devices are slightly higher than those from gas and fuel oil-fired sources. In some cases inorganic HAP emissions (i.e. metals) can be significantly higher than for these other two fuel types. These emission factors are documented in the September 22, 1997 report entitled "Development of Toxics Emission Factors for Petroleum Industrial Combustion Sources" by D. W. Hansell and G. C. England, that is available in the ICCR docket.

Given the lack of emissions data, it was not possible to perform a detailed analysis of HAP emissions versus parameters such as fuel type, operating load,

⁵ For the purposes of this subcategory, residual oil is considered as Nos. 5 and 6 oil.

stoichiometric ratio, etc. as was done for the process heater gas subcategory. An evaluation of potential above-the-floor stack controls, as well as pollution prevention aspects remains to be conducted.

Existing Sources: After evaluating the inventory and emissions data currently available, a "best performing" 12% of existing sources could not be identified. As a result, at this time there appears to be no MACT floor for this subcategory. An above-the-floor analysis for this subcategory, including pollution prevention aspects, remains to be conducted.

New Sources: A new source MACT analysis for this subcategory remains to be conducted.

VIII. MACT Determination for the Process Heater Wood Fuel Subcategory

To be completed.

IX. MACT Determination for the Process Heater Coke Oven Gas Fuel Subcategory

Conclusion: After evaluating the inventory data currently available, a best performing 12 percent of existing sources could not be identified. As a result, at this time there appears to be no MACT floor for this subcategory. An above-the-floor analysis for this subcategory, including pollution prevention aspects, has not yet been conducted.

At the July 30, 1998 Process Heaters Work Group meeting, representatives from the coke industry reviewed the coke manufacturing process, and characterized the HAP emissions anticipated from the combustion of coke oven gas generated via this process in process heaters. Their presentation and associated documentation can be found in the minutes from this meeting.

A review of the inventory database on process heaters firing coke oven gas did not identify any sources that were controlled for HAPs. Although actual HAP emissions test data were limited, the data presented on the chemical composition of the gas, its combustion properties, and the emissions of volatile organic compounds and particulate matter strongly suggest that HAP emissions from the combustion of coke oven gas should be equivalent to that of gas. Consequently, the Work Group believes that the MACT floor for coke oven gas is no control.

A question was raised regarding the disposition of mercury that occurs naturally in the coal from which the gas is derived via the coking process. It is believed by the industry that the majority of the mercury stays with the coke and tar products, and the rest is removed from the gas during the manufacturing and recovery process. According to the industry, EPA-OAQPS plans to conduct emission testing of coke oven gas in the near future. These tests should help in answering this question and completing the MACT analysis for this subcategory.

X. Discussion on Emissions Variability

Conclusion: Considerable variability is observed in the reported emissions of HAPs from similar sources firing similar fuels under similar operating conditions. This level of variability is not uncommon in databases of this type and is to be expected when searching for trace emissions at the limits of detection. The variability in the emissions database arises from the inherent variability in the combustion and measurement processes. This variability is magnified in the field due to differences in sampling and analytical methods, to differences in design, operational parameters, and location, as well as to the level of data quality assurance screening.

When analyzing the process heater and boilers emissions information, one observes that there is considerable variability in the reported emissions of hazardous air pollutants from similar sources firing similar fuels under similar operating conditions. When looking at any process, there is a natural variability that is inherent to both the process and the device used to measure the process. The vast majority of this variability is most likely due to sampling and analytical errors. Some small portion of the variability may be due to minor differences in the design, operation, and geographic location of the combustion devices.

An instructive demonstration of this inherent variability can be found in the PERF 92-19 study. As shown in Figure 13, variability of up to two orders of magnitude can exist even in situations where the combustion device, the measurement techniques, and the operating parameters are highly standardized. This exceedingly high quality data illustrates what might be called the “irreducible minimum” or “inherent” variability that is unavoidable when searching for trace HAP emissions at the limit of detection of the most sophisticated of sampling and analytical methods.

The PERF HAPs emission data were collected at the Sandia National Laboratory, Livermore, California, Combustion Research Facility’s Burner Engineering Research Laboratory (BERL), a 2.0 MMBtu/hr test facility for full-scale industrial burners. Before and after each of the five different full-scale commercial burner test sequences, “Regulatory Base Case” repetitions were carried out to make sure that nothing in the physical setup had changed in the interim between sequences nor over the period of days required to complete a given test sequence. While this was done primarily to make sure that “the same” system was being tested each time, this procedure of Regulatory Base Case repetition provides the concomitant benefit of demonstrating the irreducible minimum data variability for trace HAPs.

The PERF “Regulatory Base Cases” characterized normal operation at 2 MMBtu/hr at a stoichiometric ratio of 1.25 (i.e., 25% excess air) and furnace exit temperature 1600F firing either refinery fuel gas, the “A1” cases, or natural gas, the “A4” cases. The Regulatory Base Case “A1” fuel was a mixture of 16% hydrogen in natural gas plus propane to yield 1050 Btu/scf heating value, while the Regulatory Base Case “A4” was pure natural gas with the same heating value of 1050 Btu/scf. Thus the Regulatory Base Case fuel mixtures, heating value, burner load, stoichiometric ratio and furnace exit temperature were all duplicated at each repetition as nearly as possible and in strict conformance with the highest EPA QA/QC protocols. The PERF 92-19 CRADA’s

Quality Assurance Project Plan, acknowledged by EPA as one of the best the Agency had ever seen, guaranteed data of regulatory development quality.

As the sampling, analytical, and operating conditions at the BERL were more tightly controlled than would be possible in a field facility, the data from this study provides a benchmark for HAP emissions data variability. For example, one test team, on the same combustion device, using the same sampling and analytical methods conducted at the same laboratories, collected all of the data. Yet even under these highly controlled conditions, substantial "inherent" HAP emissions data variability was observed.

This inherent variability that is observed even under the most controlled situations is magnified and added to in the field by many other sources of variability. These sources include differences in sampling and analytical procedures, detection limits, sample volumes, analytical accuracy and precision requirements, lab contamination, data reporting requirements, different sampling contractors, data reduction and data entry errors, etc. Many of these variables are listed in Table 5 found at the end of this Section. This table shows selected HAPs sampling and analytical procedures, detection limits, and acceptable analytical accuracy and precision requirements. As the table illustrates, accuracy errors and imprecisions of up to 50% are allowed by many methods. These allowances will contribute to variability in measurements.

In databases such as those used in the ICCR, the analytical procedure is the parameter that can be expected to have a large impact on the emissions variability. This is due to the fact that non-detect data are generally reported as either the full or one-half the detection limit. Thus, units with emissions below detectable levels will have very different reported emissions if they are tested by two methods with different detection limits.

For example, the detection limit for the polycyclic aromatic hydrocarbon benzo(a)pyrene is a factor of 200 lower if the sample is analyzed using high resolution gas chromatography (GC)/high resolution mass spectrometry (MS) rather than low resolution GC/low resolution MS. Therefore, if two similar sources are tested for benzo(a)pyrene, one using the high resolution technique and the other using the low resolution technique, and benzo(a)pyrene is not detected in either sample, the reported emissions will be 200 times higher for the source tested with the low resolution technique even if all other sources of variability are equivalent. Both techniques are valid; however the low resolution technique is less expensive.

Another factor that impacts variability is the level of data quality assurance screening. The U.S. EPA has procedures for addressing low sensitivity, non-detect data and determining and eliminating outliers. For example, the WSPA/API/CARB database has undergone such a screening which has to some extent lowered the overall variability. The ICCR Emissions Database has not undergone such a screening procedure.

To a much lesser extent, differences in process heater design, in process operating conditions, and even in the location of combustion systems can contribute to the emissions data variability. For example, operational parameters such as swings in process feed rates and in load changes brought about by interactions with other processes could impact the

variability. A combustion system located in a hot, humid climate may be operated differently than a system in a cold, dry climate. Differences can even be expected based upon changes in season (i.e. between winter and summer).

Even if each of these many different aspects by themselves contributes only a small percentage of the overall variability, together they can add up to orders-of-magnitude differences in the measured emissions across the population of sources as observed in this MACT determination analysis. Lastly, it should be mentioned that a quantitative assessment of the relative contribution of the various factors discussed in this Section is not possible based on the information available in the ICCR databases.

Table 5. Selected HAPs Sampling and Analytical Procedures and Detection Limits

HAP	Sampling &	Sampling	Analytical	Detection	Detection Limit	Analytical	Analytical
PAH - Benzo(a)pyrene	CARB 429	Isokinetic with XAD-2 resin	HRGC/HR MS	5	2.7E-09	+/- 50	50-150
PAH - Benzo(a)pyrene	CARB 429	Isokinetic with XAD-2 resin	HRGC/LR MS	100	5.4E-08	+/- 50	50-150
PAH - Benzo(a)pyrene	EPA SW-846 M0010/ EPA	Isokinetic with XAD-2 resin	LRGC/LR MS	1,000	5.4E-07	+/- 50	50-150
Formaldehyde		Hot wet extraction	FTIR	120,000	6.8E-05		
Formaldehyde	CARB 430	Non-isokinetic with DNPH	HPLC	10,000	5.4E-06	+/- 10	70-130
Formaldehyde	EPA SW-846 M0011/ EPA	Isokinetic with DNPH	HPLC	800	4.4E-07		
Benzene	EPA SW-846 M0030/ EPA	Non-isokinetic with Tenax	GC/MS	1,000	5.4E-07	+/- 50	50-150
Benzene	EPA Method 18	Non-isokinetic with Tedlar	GC/PID/E CD	160,000	8.8E-05	+/- 5	90-110
Benzene	CARB 410A	Non-isokinetic with Tedlar	GC/PID	11,000	5.8E-06	+/- 5	90-110
Benzene	CARB 410A	Non-isokinetic with Tedlar	GC/FID/PI D	3,200	1.8E-06	+/- 5	90-110
Benzene	EPA SW-846 M0040/EPA	Non-isokinetic with Tedlar	GC/MS	1,600	8.8E-07	+/- 25	70-130
Benzene			FTIR	320,000	1.8E-04		
PCDD/PCDF- 2,3,7,8-TCDD	EPA Method 23	Isokinetic with XAD-2 resin	HRGC/HR MS	0.005	2.7E-12		
PCDD/PCDF- 2,3,7,8-TCDD	CARB 428	Isokinetic with XAD-2 resin	HRGC/HR MS	0.005	2.7E-12	+/- 30	60 - 140
PCDD/PCDF- 2,3,7,8-TCDD	EPA SW-846 M0010/ EPA	Isokinetic with XAD-2 resin	HRGC/HR MS	0.05	2.7E-11		
PCDD/PCDF-	EPA SW-846	Isokinetic with	HRGC/LR	50	2.7E-08		

1. Based on 1.0 dscm sample volume for isokinetic methods and 20 liter sample volume for CARB 430 and EPA SW-486 M0030.
2. Based on 1.0 dscm sample volume for isokinetic methods and 20 liter sample volume for CARB 430 and EPA SW-486 M0030 and unit firing natural gas.

ECD - Electron capture detector
FID - Flame ionization detector
FTIR - Fourier transform infrared spectroscopy
GC - Gas chromatography
HPLC - High pressure liquid chromatography
HRGC - High resolution gas chromatography
HRMS - High resolution mass spectrometry
LRGC - Low resolution gas chromatography
LRMS - Low resolution mass spectrometry
MS - Mass spectrometry
PID - Photo ionization detector

09/04/98

**ICCR PROCESS HEATER DATABASE
ANALYSIS FLOW DIAGRAM**
(posted as a separate file: dbflow2)